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A new approach to understanding the mechanism of dolomitization: Time-resolved X-ray diffraction of the calcite-to-dolomite transformation

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Dolomitization altered vast volumes of limestone during the Phanerozoic, but the (bio)geochemical and hydrologic pathways that governed diagenesis remain hotly debated. Although dolomite is thermodynamically more stable than calcite in modern marine waters, efforts to crystallize long-range ordered, stoichiometric dolomite at ambient temperature and pressure have largely been unsuccessful. The dolomitization process occurs as two steps: from calcite (*S.G. R-3c*) to protodolomite (PD, *S.G. R-3c)*, which in turn evolves to ordered dolomite (OD, *S.G. R-3*). It is still controversial whether cation ordering occurs by dissolution-reprecipitation or solid-state diffusion.

Here, we conducted time-resolved X-ray diffraction (TRXRD) and transition electron microscopy (TEM) studies of the transformation of synthetic calcite to ordered dolomite. Our TRXRD experiments were performed by placing powdered calcite in 1-mm quartz-glass capillaries containing 1 *M* $CaCl_2$: 1 *M* $MgCl_2$ solutions and heating to temperatures ranging from 160-220 °C. Rietveld analysis of the TRXRD data revealed that: 1) The onset of protodolomite formation coincided with the loss of calcite peak intensity; 2) Ordered dolomite diffraction peaks appeared when refined calcite abundance dropped below ~10 wt%; 3) The Ca occupancy (Ca_{occ} = Ca/(Mg+Ca)) for PD refined to ~0.4 for the first PD precipitate, increased to ~0.6, and during the transformation to OD, converged to 0.5. 4) At 160 °C, the reaction kinetics were too slow for OD to form, and the Ca_{occ} plateaued at ~0.6. These results suggest that 1) the presence of calcite may inhibit the formation of OD; and 2) a Ca composition of ~60 mol% may be an indicator of a highly evolved, rather than an immature, *R-3c* protodolomite.